

Observation of a level crossing in a molecular nanomagnet using implanted muons

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Abstract. We have observed an electronic energy level crossing in a molecular nanomagnet (MNM) using muon-spin relaxation. This effect, not observed previously despite several muon studies of MNM systems, provides further evidence that the spin relaxation of the implanted muon is sensitive to the dynamics of the electronic spin. Our measurements on a broken ring MNM [$\text{H}_2\text{N}^t\text{Bu}^{is}\text{Pr}][\text{Cr}_8\text{CdF}_9(\text{O}_2\text{CC}(\text{CH}_3)_3)_{18}]$ (hereafter Cr₈Cd), which contains eight Cr ions, show clear evidence for the $S = 0 \rightarrow S = 1$ transition that takes place at $B_c = 2.3$ T. The crossing is observed as a resonance-like dip in the average positron asymmetry and also in the muon-spin relaxation rate, which shows a sharp increase in magnitude at the transition and a peak centred within the $S = 1$ regime.

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Molecular nanomagnets (MNMs) [1] comprise clusters of transition metal ions. Strong exchange coupling between these ions within a single molecule results in each molecule possessing a ground state described by a total spin eigenvalue S . Excited states will possess other values of S and the splitting of these levels in an applied magnetic field often leads to level crossings in which an excited spin state in zero field becomes the new ground state at fields above the field at which a crossing occurs. MNMs have been widely studied in recent years, most recently in anticipation of their possible deployment as elements of quantum computers [2], although much interest also centres on the quantum tunnelling of the magnetization (QTM) which can take place when the magnetic energy levels are at resonance [1]. When implanted muons were first used to probe the spin dynamics in these systems, it was hoped that they would be sensitive to level crossings. However, early studies failed to observe any signature of such crossings [3] and, despite the possible observation of effects ascribed to a matching of the MNM electronic energy level splitting with that of the muon hyperfine levels [4] and the observation of crossings in broadly related systems [5], the observation of a crossing in a MNM has remained elusive until now. Here we demonstrate that muons are sensitive to the electronic energy level crossings in MNMs. Our measurements on a broken ring system, made using the new HiFi spectrometer at the ISIS facility, demonstrate the effect of the level crossing on the integrated positron asymmetry and on the muon-spin relaxation rate.

The material measured in this study is related to the octonuclear system $[\text{Cr}_8\text{F}_8(\text{O}_2\text{CC}(\text{CH}_3)_3)_{16}]$ [6]. That material has a $S = 0$ ground state due to antiferromagnetic coupling ($J_{\text{Cr}-\text{Cr}} \approx 16.9$ K) between the eight nearest neighbour Cr^{3+} ($s = 3/2$) spins. In contrast, the broken ring system Cr_8Cd [7] (full formula $[\text{H}_2\text{N}^t\text{Bu}^{\text{is}}\text{Pr}] [\text{Cr}_8\text{CdF}_9(\text{O}_2\text{CC}(\text{CH}_3)_3)_{18}]$, shown in figure 1(a)) has one $s = 0$ Cd^{2+} ion added to the ring which interrupts the strong intraring exchange interactions, effectively disconnecting two Cr^{3+} spins and changing the topology of the magnetic interactions [8]. This has the effect of significantly altering the bulk magnetic behaviour of the system, whose first level crossing ($S = 0 \rightarrow S = 1$) occurs at a magnetic field of $B_c = 2.3$ T (compared to 7.3 T for Cr_8).

In a muon-spin relaxation ($\mu^+\text{SR}$) experiment [9], spin-polarized positive muons are stopped in a target sample. The time evolution of the muon spin polarization is probed via the positron decay asymmetry function $A(t)$ to which it is proportional. Our $\mu^+\text{SR}$ measurements were made on the new HIFI spectrometer [10, 11] at the ISIS facility, Rutherford Appleton Laboratory, UK. This instrument allows the application of magnetic fields of up to $B = 5$ T, longitudinal to the initial muon spin direction and is optimised for time-differential muon spin relaxation studies at a pulsed muon source. For the measurements, six crystallites of Cr_8Cd , prepared as reported previously [7], were arranged on a silver plate attached to the cold-finger of a dilution refrigerator. The crystallites were aligned such that their a -axes were directed perpendicular to the direction of the applied field.

Example data measured at $T = 70$ mK are shown in figure 1(b) for two values

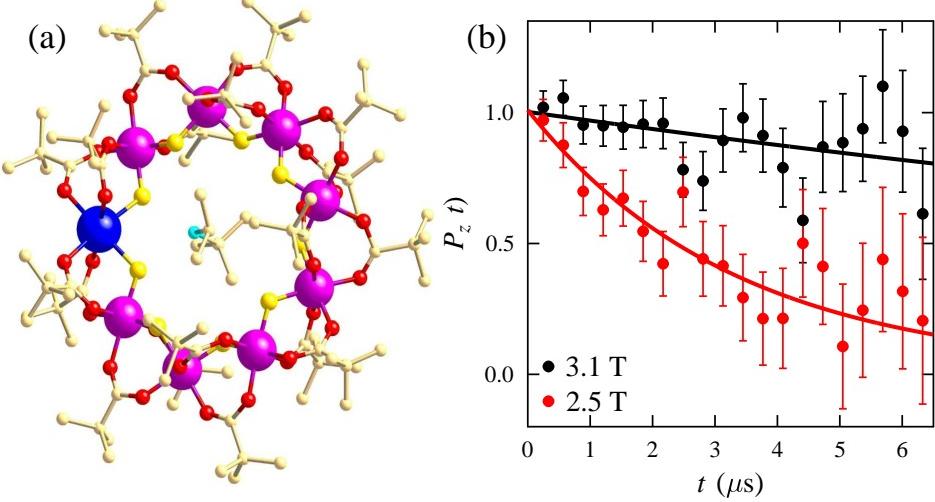


Figure 1. (a) The Cr₈Cd molecule. (b) Example muon-spin relaxation spectra measured at 70 mK in applied longitudinal magnetic field.

of applied magnetic field. The muon polarization $P_z(t)$ (which is proportional to the positron asymmetry) is seen to decrease monotonically and is well described by an exponential relaxation function. This is typical behaviour for these MNM systems [12], and can be attributed to dynamic fluctuations of the local magnetic field distribution at the muon sites in the material [13]. In order to follow the behaviour probed by the muon across the level crossing in Cr₈Cd we plot the time-averaged asymmetry in figure 1(b) for scans in applied field at temperatures of 70 mK and 20 K. Resonance-like minima are clearly observable, which may be identified with the electronic energy level crossing between $S = 0$ and $S = 1$ ground states. At 70 mK the minimum occurs at $B = 2.29$ T with a FWHM of approximately 0.4 T. Increasing the temperature causes the resonance to broaden in an asymmetric fashion and shifts the minimum to a slightly higher field of 2.35 T.

Another method of examining the resonance is to fit the time-differential spectra to the functional form

$$A(t) = A_{\text{rel}}e^{-\lambda t} + A_{\text{bg}}, \quad (1)$$

where A_{rel} is the relaxing amplitude and A_{bg} is the background contribution, which we expect to be highly field-dependent due to the effect of the magnetic field on the incoming muons and outgoing positrons due to the Lorentz force. The amplitude A_{rel} was held fixed throughout the fitting procedure and the extracted relaxation rate λ , measured at 70 mK is shown in figure 2(b). The relaxation rate is seen to increase sharply around B_c and peak at $B = 2.54$ T. Note that the peak is observed well within the $S = 1$ regime. (The origin of the apparent broad, low-amplitude peak in the low-field region is unclear, although this most-likely represents a background contribution to the relaxation.)

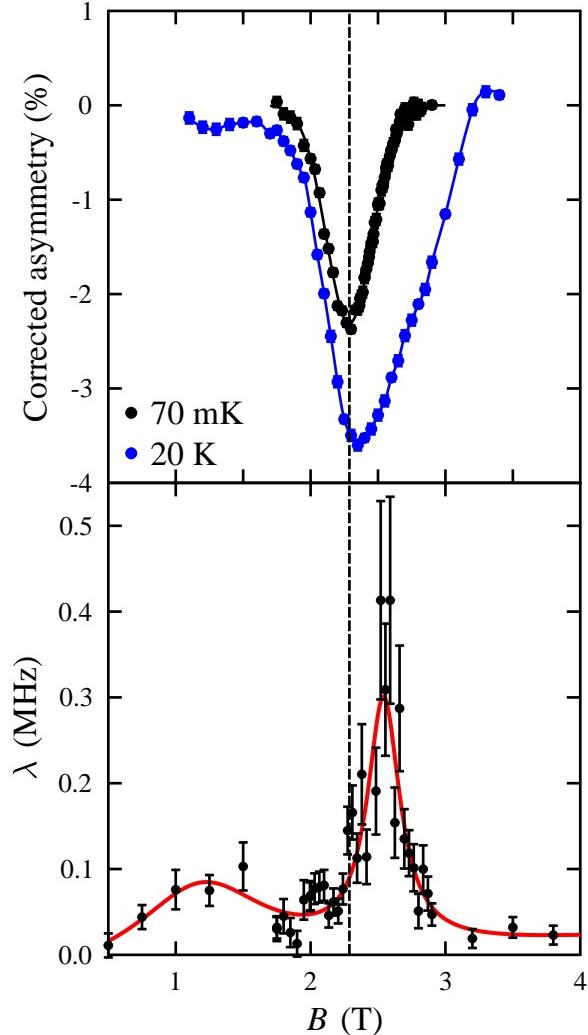


Figure 2. (a) Average asymmetry (corrected for background) as a function of applied magnetic field measured at 70 mK and 20 K. Resonance-like minima are observed at the level crossing. (b) Relaxation rate λ at 70 mK resulting from fitting the measured spectra to equation (1). The peak is displaced to slightly higher fields than the level crossing.

Our previous study of MNM systems[12] identified the mechanism through which the muon spin is relaxed in these materials. Specifically, measurements on Cr₈ and on the related $S = 1$ MNM system Cr₇Mn showed that the muon spin ensemble is relaxed by static nuclear magnetism in $S = 0$ systems such as Cr₈ and by the large electronic spin in $S \neq 0$ MNMs such as Cr₇Mn. Moreover, a large difference in relaxation rates between protonated and deuterated samples demonstrates that the proton fluctuations are largely responsible for the dephasing of the large MNM electronic spin that we detect with muons at low temperatures. It is likely, therefore, that for our level crossing measurement of Cr₈Cd, the channels through which the muon spins are relaxed change

quite dramatically from weak nuclear relaxation in the $S = 0$ regime to strong electronic relaxation upon traversing the level crossing to the $S = 1$ regime above B_c . Although it is probable that the fluctuation rate of the net moment of a molecule is symmetrically peaked about the crossing, the effective coupling of the muon to the electronic spins on the molecule is likely to be smoothly turned on upon crossing into the $S = 1$ regime and this may cause the peak in the muon response to be shifted to slightly higher fields, as we observe. Another possibility for the shift is that the electronic fluctuation rate lies outside the muon time window close to the transition, but slows above the crossing causing the maximum in λ as it decends into the regime in which the muon is sensitive.

In conclusion, muon-spin relaxation has been shown to be sensitive to the level crossing in the molecular nanomagnet Cr₈Cd. This opens up possibilities for its use in probing such crossings in other systems. Future work will involve examining the crossings between two $S \neq 0$ states in order to further examine the nature of the coupling of the muon to the molecules.

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